



PCT

特許協力条約に基づいて公開された国際出願

| | | |
|--|----|---|
| (51) 国際特許分類6 C09K 9/02, C08F 2/46, C08K 5/15, C08L 33/14, G02C 7/02, G03C 1/73 | A1 | (11) 国際公開番号 WO96/37573 (43) 国際公開日 1996年11月28日 (28.11.96) |
| (21) 国際出願番号 PCT/JP96/01384 (22) 国際出願日 1996年5月24日 (24.05.96) (30) 優先権データ 特願平7/128145 1995年5月26日 (26.05.95) JP (71) 出願人 (米国を除くすべての指定国について) 株式会社 トクヤマ(TOKUYAMA CORPORATION)[JP/JP] 〒745 山口県徳山市御影町1番1号 Yamaguchi, (JP) (72) 発明者; および (75) 発明者/出願人 (米国についてののみ) 伊村智史(IMURA, Satoshi)[JP/JP] 西竹敏博(NISHITAKE, Toshihiro)[JP/JP] 〒745 山口県徳山市御影町1番1号 株式会社 トクヤマ内 Yamaguchi, (JP) (74) 代理人 弁理士 大島正孝(OHSHIMA, Masataka) 〒160 東京都新宿区四谷4丁目3番地 福屋ビル 大島特許事務所 Tokyo, (JP) | | (81) 指定国 AU, JP, SG, US, 欧州特許(AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). 添付公開書類 国際調査報告書 |
| (54) Title : PROCESS FOR THE PRODUCTION OF PHOTOCHROMIC PRODUCT OF CURING (54) 発明の名称 フォトクロミック硬化体の製造方法 (57) Abstract A photochromic product of curing is produced by irradiating a photopolymerizable composition comprising: (A) a radical-polymerizable monomer, (B) an ultraviolet polymerization initiator exhibiting a main absorption in the ultraviolet region and a molar absorption coefficient of 150 l/(mol.cm) or above at 400 nm, and (C) a photochromic compound with an active energy radiation exhibiting an emission spectrum at 400 nm or above as the main spectrum to cure the composition. The above composition can easily be polymerized in a short time to give a product of curing exhibiting excellent photochromism. | | |

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明 細 書

フोटクロミック硬化体の製造方法

5 技術分野

本発明は、光重合法により重合硬化し、その硬化体が良好なフोटクロミック性を示すフोटクロミック硬化体を製造する方法に関する。

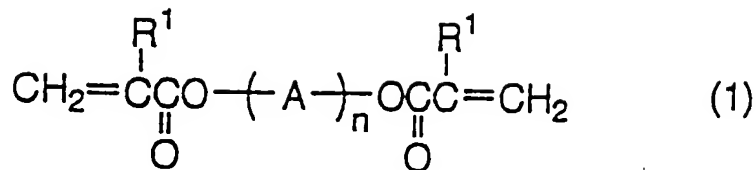
背景技術

10 フोटクロミズムとは、ここ数年来注目を引いてきた現象であって、ある化合物に太陽光あるいは水銀灯の光のような紫外線を含む光を照射すると速やかに色が変わり、光の照射を止めて暗所におくと元の色にもどる可逆作用のことである。この性質を有する化合物はフोटクロミック化合物と呼ばれ、従来から種々の構造の化合物が合成されてきたが、
15 その構造には特別な共通の骨格は認められない。

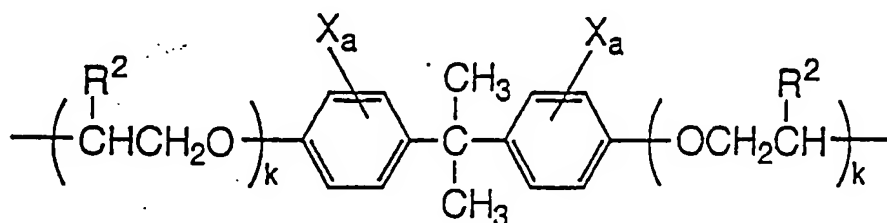
フोटクロミック性を示す硬化体は、上記フोटクロミック化合物をあらかじめ成形した重合体の表面に被覆させる方法、あるいはラジカル重合性単量体に該フोटクロミック化合物を溶解させた後重合硬化させる方法等によって得られる。

20 さて、ラジカル重合性単量体を重合させる方法としては、一般に熱により重合を進行させる方法と、光により重合を進行させる方法が知られている。ところが、このフोटクロミック性を示す硬化体を得る場合において、光重合法は含有されるフोटクロミック化合物が光重合開始剤の開裂に必要な紫外線を吸収することおよび光の照射によるフोटクロミック化合物自身の発色によって光の透過が阻害されること等から、
25 ラジカル重合性単量体の好適な重合が望めない。また、本発明者らの知見によれば、光重合法の採用により重合不十分なマトリックス重合体中にフोटクロミック化合物が分散する場合、該フोटクロミック化合物の耐久性が著しく低下する。

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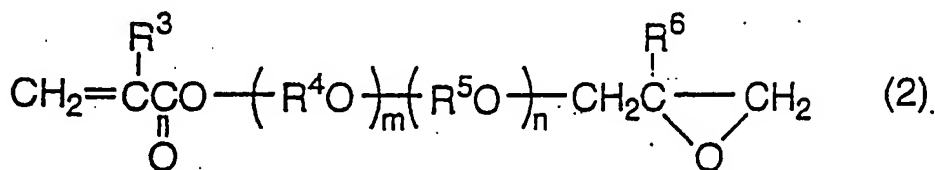


ここで、 R^1 はそれぞれ同種または異種の水素原子またはメチル基であり、 A は同種または異種の置換されてもよいアルキレン基、オキシアルキレン基または下記式

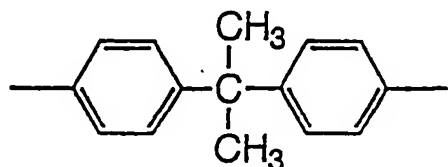


(但し、 R^2 は水素原子またはメチル基であり、 X はハロゲン原子であり、 k は0～5の整数であり、 a はハロゲン原子の置換数を示す0～4の整数である。)であり、 n は1～20の整数である、
で示されるジアクリレート化合物またはジメタクリレート化合物。

下記式 (2)



ここで、 R^3 および R^6 は、それぞれ同種または異種の水素原子またはメチル基であり、 R^4 および R^5 は、それぞれ同種または異種の置換されていてもよいアルキレン基または下記式



で示される基であり、 m および n は0または1である、

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トおよびビスフェノール A-モノグリシジルエーテルメタクリレート等が挙げられる。

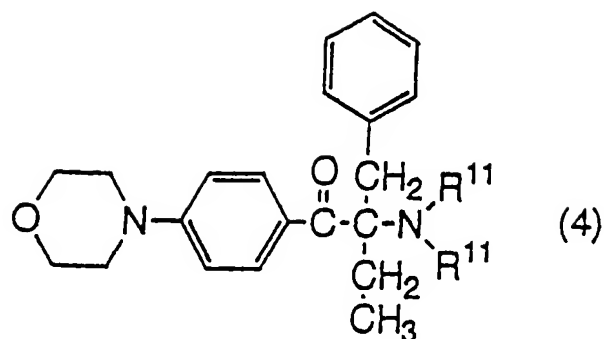
ビニルベンジル化合物としては、例えばビス-4-ビニルベンジルエーテル、ビス-4-ビニルベンジルスルフィド、1,2-(p-ビニルベンジルオキシ)エタン、1,2-(p-ビニルベンジルチオ)エタン、ビス-(p-ビニルベンジルオキシエチル)スルフィド等が挙げられる。

その他、ラジカル重合性単量体としては、不飽和カルボン酸、アクリル酸およびメタクリル酸エステル、フマル酸エステルおよび芳香族ビニル化合物を用いることもできる。かかる不飽和カルボン酸化合物としては、例えばアクリル酸、メタクリル酸、無水マレイン酸、フマル酸、アクリル酸を、メタクリル酸エステルとしては、例えばアクリル酸メチル、メタクリル酸メチル、メタクリル酸ベンジル、メタクリル酸フェニル、トリブロモフェニルメタクリレート、2-ヒドロキシエチルメタクリレート、トリフロロメチルメタクリレート、ウレタンアウリレートを、フマル酸エステルとしては、例えばフマル酸モノメチル、フマル酸ジエチル、フマル酸ジフェニルを、そして芳香族ビニル化合物としては、例えばスチレン、クロロスチレン、 α -メチルスチレン、ビニルナフタレン、イソプロベニルナフタレン、プロモスチレン、ジビニルベンゼン等を挙げることができる。これらのラジカル重合性単量体は一種または二種以上を混合して用いてもよい。

上記ラジカル重合性単量体の中でも、後述のフォトクロミック化合物とラジカル重合性単量体との混合物を光重合して得られる硬化体のフォトクロミック性の耐久性および発色-消色等の物性を勘案すれば、前記一般式(1)で示されるジアクリレート化合物またはジメタクリレート化合物と、一般式(2)で示されるエポキシ基含有アクリレート化合物またはメタクリレート化合物とを混合したラジカル重合性単量体混合物を用いることが好ましい。

本発明においては、紫外領域に主吸収があり且つ400nmにおけるモル吸光係数が150リットル/(mol \cdot cm)以上である紫外線重

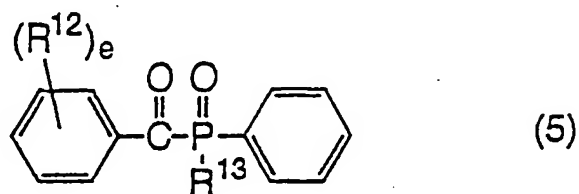
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ここで、複数の R^{11} は同一もしくは異なり、メチル基またはエチル基である、

で表わされる α -アミノアルキルフェノン系化合物。

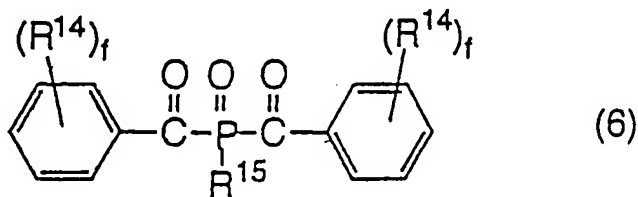
5 下記式 (5)



ここで、複数の R^{12} は同一もしくは異なり、メチル基、メトキシ基または塩素原子であり、 e は 2 または 3 であり、 R^{13} はフェニル基またはメトキシ基である、

10 で表わされるアシルフォスフィンオキシド系化合物。

下記式 (6)



ここで、複数の R^{14} は同一もしくは異なり、メチル基、メトキシ基または塩素原子であり、 f は 2 または 3 であり、 R^{15} は 2, 4, 4-トリメチルペンチル基である、

で表わされるビスアシルフォスフィンオキシド系化合物。

本発明において、紫外領域に主吸収があり且つ 400 nm におけるモ

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さらに、これら紫外線重合開始剤に加え、熱重合開始剤を添加してもよい。添加できる熱重合開始剤としては、公知のものが制限なく使用できる。該熱重合開始剤としては、ベンゾイルパーオキサイド、ラウロイルパーオキサイド等のジアシルパーオキサイド；*t*-ブチルパーオキシネオデカネート等のパーオキシエステル；ジイソプロピルパーオキシジカーボネート等のパーカーボネート；アゾビスイソブチロニトリル等のアゾ化合物等が挙げられる。

本発明に用いる光重合性組成物に含有されるフォトクロミック化合物としては、その発色時の吸収が可視光域にあるものであればなんら制限なく使用できる。可視域の吸収を具体的に示すと、400～480 nm付近の吸収特性を示すフォトクロミック化合物は黄色からオレンジ色の発色色調を示し、480～550 nm付近に吸収特性を示すフォトクロミック化合物は赤色から紫色の発色色調を示し、550～600 nm付近に吸収特性を示すフォトクロ化合物は紫～青色の発色色調を示す。これらフォトクロミック化合物は単独で用いてもよいが二種以上組み合わせることによって グレー、ブラウンおよびアンバーといった中間色の発色色調を得ることもできる。

本発明において好適に使用されるフォトクロミック化合物としては、クロメン化合物、フルギドまたはフルギミド化合物およびスピロオキシジン化合物を挙げることができる。

クロメン化合物としては、クロメン骨格を有し、フォトクロミック性を有する公知の化合物を何等制限なく使用することができ、具体的には下記化合物が例示される。

クロメン化合物；

- ① 2,2-ジフェニル-7-オクトキシ(2H)ベンゾ(f)クロメン
- ② スピロ(ビシクロ[3.3.1]ノナン-9,2'-(2H)ベンゾ(h)クロメン)
- ③ スピロ(ノルボルナン-2,2'-(2H)ベンゾ(h)クロメン)
- ④ 7'-メトキシスピロ(ビシクロ[3.3.1]ノナン-9,2'-(2H)ベンゾ(h)クロメン)

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スピロオキサジン化合物；

① 1,3,3-トリメチル-スピロ (インドール-2,3-[3,2-a]

[1,4] ナフトオキサジン

② 1,3,3-トリメチル-6'-ピペリジノ-スピロ (インドール-
2,3-[3,2-a] [1,4] ナフトオキサジン③ 6-フルオロ-1'-メチル-8''-メトキシ-6''-モルホリノ
ジスピロ (シクロヘキサン-1,3'-(3H) インドール-2'-
(2'H), 3''-(3H) ナフト (3,2-a) (1,4) オキサジ
ン)④ 1'-メトキシカルボニルメチル-8''-メトキシ-6''-(4-メ
チルピペラジノ) ジスピロ (シクロヘキサン-1,3'-(3H) イ
ンドール-2'-(2'H), 3''-(3H) ナフト (3,2-a)
(1,4) オキサジン)⑤ 1'-(2-(ジオキサン-2-イル) エチル)-6''-モルホリノ
ジスピロ (シクロヘキサン-1,3'-(3H) インドール-2'-
(2'H), 3''-(3H) ナフト (3,2-a) (1,4) オキサジ
ン)⑥ 5-フルオロ-1'-メチル-6''-ピペリジノジスピロ (シクロヘ
キサン-1,3'-(3H) インドール-2'-(2'H), 3''-(3
H) ナフト (3,2-a) (1,4) オキサジン)⑦ 8''-メトキシジスピロ (シクロヘキサン-1,3'-(3H) イン
ドール-2'-(2'H), 3''-(3H) ナフト (2,3-a) (1,
4) オキサジン)

フォトクロミック化合物の添加量としては、発色時の濃度に応じて適
宜選択すればよいが、通常はラジカル重合性単量体100重量部に対し
て、0.001~1.0重量部、好ましくは0.01~0.5重量部の範囲
である。フォトクロミック化合物の添加量が、0.001重量部未満では、
十分な発色濃度が得られず、またフォトクロミック特性の耐久性が低下
してしまう。1.0重量部を越えるところでは、短時間で重合が完結しづ

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でき、紫外線重合開始剤を開裂できるので、十分重合硬化が進行する。

照射時間は、光源の波長や強度、硬化体の形状や構成成分によって異なるため、予備的な実験等によって予め決定しておくのが望ましい。

光重合を行う場合は、鋳型の少なくとも光照射する面は透明であることが必要であり、一般的にこの部分にはガラス等が使用される。特に石英ガラス等の紫外線を透過しやすい材質が好ましいが、透明であれば材質には限定されない。また、成形時に外部から圧力をかけながら重合してもなんら差し支えない。

本発明の製造方法は、公知の注型重合方法に採用することができる。代表的な方法を例示すると、エラストマーガスケットまたはスペーサーで保持されているモールド間に光重合性組成物を注入し、前記活性エネルギー線を照射して硬化させた後取り出す。

本発明の方法で得られるフォトクロミック硬化体は、その用途に応じてさらに以下のような処理を施すこともできる。即ち、分散染料等を用いる染色、シランカップリング剤やケイ素、ジルコニウム、アンチモン、アルミニウム、スズ、タングステン等のゾル成分を主成分とするハードコート剤や、 SiO_2 、 TiO_2 、 ZrO_2 等の金属酸化物の薄膜の蒸着や有機高分子の薄膜の塗布による反射防止処理、帯電防止処理等の加工および2次処理を施すことも可能である。

本発明の光重合法による製造方法の採用により、短時間でフォトクロミック化合物の劣化がなく、発色濃度が高くしかも十分な硬度を持つフォトクロミック硬化体を得ることができ、得られた硬化体は太陽光もしくは水銀灯の光のような紫外線を含む光で無色から着色状態に変化し、その変化が可逆的で優れた調光性を有している。従って、得られる硬化体は、フォトクロミック性を有する有機硝子として有用であり、例えばフォトクロミックレンズの用途に好適に使用することができる。

実施例

以下、本発明を説明するために、実施例を挙げて説明するが、本発明

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F 2 : N-シアノメチル-6,7-ジヒドロ-4-メチル-2-フェニルスピロ(5,6-ベンゾ[b]チオフェンジカルボキシイミド-7,2-トリシクロ[3.3.1.1]デカン

スピロオキサジン化合物:

5 S 1 : 1,3,3-トリメチル-スピロ(インドール-2,3-[3,2-a][1,4]ナフトオキサジン

S 2 : 1,3,3-トリメチル-6'-ビペリジノ-スピロ(インドール-2,3-[3,2-a][1,4]ナフトオキサジン

10 光重合開始剤は下記のとおりである。〔〕内は、400nmにおけるモル吸光係数〔リットル/(mol・cm)〕を示す。

I 1 : CGI-1700 (商品名: 日本チバガイギー社製)

15 -ビス(2,6-ジメトキシベンゾイル)-2,4,4-トリメチルペンチルフォスフィンオキシド〔550〕と2-ヒドロキシ-2-メチル-1-フェニル-プロパン-1-オン〔10以下〕の1:3の混合物

I 2 : 2,4,6-トリメチルベンゾイルジフェニルフォスフィンオキシド〔250〕

I 3 : 2-ベンジル-2-ジメチルアミノ-1-(4-モルフォリノフェニル)-プロパン-1〔200〕

20 I 4 : メチルベンゾイルホルメート〔10以下〕

実施例1

25 2,2-ビス(4-メタクリロイルオキシジエトキシフェニル)プロパン90部、グリシジルメタクリレート10部、表1に示した添加量のフォトクロミック化合物および光重合開始剤を添加し十分に混合した。この混合液をガラス板とエチレン-酢酸ビニル共重合体からなるガasketで構成された鋳型の中に注入し、メタルハライドランプと鋳型の間に、実質的に400nm以上の活性エネルギー線を照射するため、紫外線カットフィルターとして、380nm:99%、390nm:98%、400nm:50%、410nm:15%の活性エネルギー線を遮断する

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観察した。以上の結果を表1に示した。

実施例 2

実施例 1 において示したフォトクロミック化合物、ラジカル重合性単量体の種類を変えて行った以外、実施例 1 と同様にした。結果を表 2 に示した。

比較例 1

光重合開始剤として、メチルベンゾイルホルメートを用いた以外は、実施例 1 と同様に実施し、結果を表 1 に示した。

比較例 2

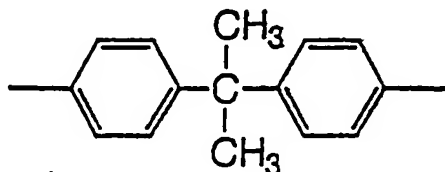
- 5 光重合開始剤として、メチルベンゾイルホルメートを用い、紫外線カットフィルターを使用しなかった以外は、実施例 1 と同様に実施し、結果を表 1 に示した。

比較例 3

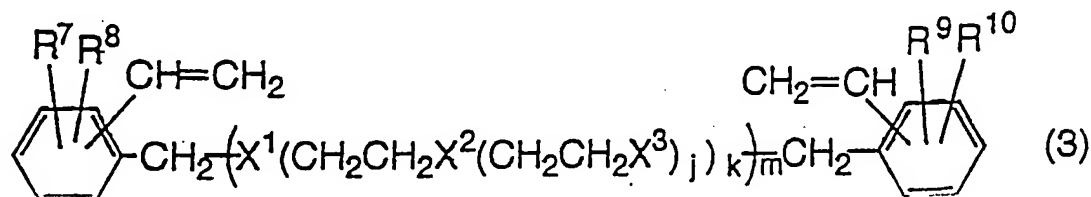
- 10 紫外線カットフィルターを使用しなかった以外は、実施例 1 と同様に実施し、結果を表 1 に示した。

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ここで、 R^3 および R^6 は、それぞれ同種または異種の水素原子またはメチル基であり、 R^4 および R^5 は、それぞれ同種または異種の置換されていてよいアルキレン基または下記式



- 5 で示される基であり、 m および n は0または1である、
 で示されるエポキシ基含有アクリレート化合物またはメタクリレート化合物並びに下記式(3)



- 10 ここで、 R^7 、 R^8 、 R^9 および R^{10} は、それぞれ同種あるいは異種のハロゲン原子であり、 X^1 、 X^2 および X^3 は、それぞれ酸素原子またはイオウ原子であり、 j 、 k および m は、それぞれ0または1であり、 $k=0$ の時は $j=0$ であり、また $m=0$ の時は $k=j=0$ であり、 $j=k=m=1$ のときに X^1 、 X^2 および X^3 が同時にイオウ原子になることはない。)

- 15 で示されるビニルベンジル化合物よりなる群から選ばれる少なくとも一種の化合物である請求項1に記載の方法。

3. 紫外線重合開始剤(B)が下記式(4)

- 25 -

4. 紫外線重合開始剤 (B) の使用量がラジカル重合性単量体 (A) 100重量部当り0.01~1重量部である請求項1に記載の方法。
5. フォトクロミック化合物 (C) がクロメン化合物、フルギド化合物フルギミド化合物およびスピロオキサジン化合物よりなる群から選ばれる請求項1に記載の方法。
6. フォトクロミック化合物 (C) の使用量がラジカル重合性単量体 (A) 100重量部当り0.001~1.0重量部である請求項1に記載の方法。
7. 400nm未満の波長の紫外線をカットするフィルターを通して活性エネルギー線を照射する請求項1に記載の方法。

A. 発明の属する分野の分類 (国際特許分類 (IPC))

Int. Cl.¹ C09K9/02, C08F2/46, C08K5/15, C08L33/14,
G02C7/02, G03C1/73

B. 調査を行った分野

調査を行った最小限資料 (国際特許分類 (IPC))

Int. Cl.¹ C09K9/02, C08F2/46, C08K5/15, C08L33/14,
G02C7/02, G03C1/73

最小限資料以外の資料で調査を行った分野に含まれるもの

国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

C. 関連すると認められる文献

| 引用文献の カテゴリー* | 引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示 | 関連する 請求の範囲の番号 |
|-----------------|--|------------------|
| P, A | JP, 7-292011, A (株式会社トクヤマ), 7. 11月. 1995 (07. 11. 95) & EP, 681018, A2 & AU, 9516590, A | 1-7 |
| | JP, 7-292011, A (株式会社トクヤマ), 20. 6月. 1995 - (23. 05. 95) (ファミリーなし) | 1-7 |
| A | JP, 4-358117, A (株式会社東京計画), 11. 12月. 1992 (11. 12. 92) (ファミリーなし) | 1-7 |

☐ C欄の続きにも文献が列挙されている。

☐ パテントファミリーに関する別紙を参照。

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「&」同一パテントファミリー文献

国際調査を完了した日

15. 08. 96

国際調査報告の発送日

27.08.96

国際調査機関の名称及びあて先

日本国特許庁 (ISA/JP)

郵便番号 100

東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)

藤原 浩子

電話番号 03-3581-1101 内線 3443

4H 9155

印

International Publication No. 96/37573 A1

Translated from Japanese by the Ralph McElroy Co., Custom Division
P.O. Box 4828, Austin, Texas 78765

Code: 102-53199

Ref. No.: TR 97-17

INTERNATIONAL PATENT OFFICE
WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY
International Patent Published On
The Basis of Patent Cooperation Pact
INTERNATIONAL PUBLICATION No. 96/37573 A1

Int. Cl⁶..:

C 09 K 9/02
C 08 F 2/46
C 08 K 5/15
C 08 L 33/14
G 02 C 7/02
G 03 C 1/73

Application No.:

PCT/JP96/01384

Application Date:

May 24, 1996

Publication Date:

November 28, 1996

Priority Data

No.

Hei 7[1995]-128145

Country:

Japan

Date:

May 26, 1995

PROCESS FOR THE PRODUCTION OF PHOTOCHROMIC PRODUCT OF CURING

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Designated Contracting States:

AU, JP, SG, US, European
Patent (AT, BE, CH, DE,
DK, ES, FI, FR, GB, GR,
IE, IT, LV, MC, NL, PT,
SE).

Attached Kokai Documents: International Search Reports

FOR INFORMATION ONLY

Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT.

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Abstract

A photochromic product of curing is produced by irradiating a photopolymerizable composition comprising: (A) a radical-polymerizable monomer, (B) an ultraviolet polymerization initiator exhibiting a main absorption in the ultraviolet region and a molar absorption coefficient of 150 l/(mol.cm) or above at 400 nm, and (C) a photochromic compound with an active energy radiation exhibiting an emission spectrum at 400 nm or above as the main spectrum to cure the composition. The above composition can easily be polymerized in a short time to give a product of curing exhibiting excellent photochromism.

Technical field

This invention pertains to a process for the production of a photochromic product of curing, which is formed by polymerization curing in photopolymerization, and which displays excellent photochromic property.

Background of the technology

Photochromism refers to a reversible action in which certain compounds make swift changes in color when irradiated by sunlight, the light of a mercury lamp, or some other light containing UV light, and the original color recovers when the light irradiation is stopped and the compound is placed in the dark. This phenomenon has attracted much attention in recent years. The compounds having this property are called photochromic compounds. Although compounds having various structures have been synthesized for this purpose, no special common skeleton has been identified in the structure.

The photochromic product of curing can be prepared using several methods, such as the method in which the aforementioned photochromic compound is coated on the surface of a premolded polymer, or the method in which the photochromic compound is dissolved in a radical polymerizable monomer, followed by polymerization curing.

There are several methods for polymerization of the radical polymerizable monomer, such as the method in which polymerization is carried out by heat, and the method in which polymerization is carried out by light. However, when the photochromic product of curing is formed, in the photopolymerization method, as the contained photochromic compound absorbs the UV light needed for cleavage of the photopolymerization initiator, and transmission of light is hampered by coloration of the photochromic compound itself, there is no way to carry out the appropriate polymerization for the radical polymerizable monomer. According to the knowledge of the present inventors, when the photopolymerization method is adopted, and the photochromic compound is dispersed in the matrix polymer with insufficient polymerization, the durability of the photochromic compound significantly deteriorates.

When the photochromic product of curing is formed in this way, the thermal polymerization method is usually adopted as the polymerization method of the radical polymerizable monomer. However, the method of thermal polymerization has a polymerization time of several hours, and the productivity of the product of curing is not satisfactory.

In light of the aforementioned background, this invention provides a method for forming a photochromic product of curing

having excellent photochromic property and allowing easy polymerization in a short time by adopting the photopolymerization method.

Disclosure of the invention

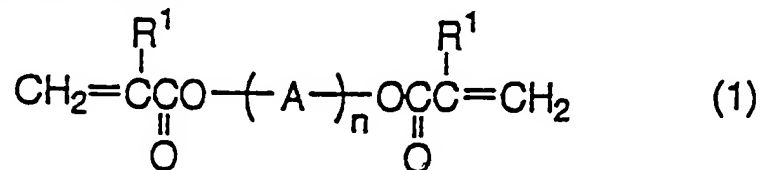
In order to solve the aforementioned problems, the present inventors have conducted extensive research. As a result of this research, it was found that by combining a prescribed type of photopolymerization initiator and an active energy radiation having a prescribed light-emission spectrum, it is possible to form the photochromic product of curing having excellent photochromic property in a short time easily. In this way, the present invention was reached.

That is, this invention provides a process for the production of a photochromic product of curing, characterized by the fact that curing is realized by radiating an active energy radiation having a 400 nm or greater light-emission spectrum onto a photopolymerizable composition containing (A) radical polymerizable monomer, (B) UV-light polymerization initiator having the main absorption in the UV region and having a molar light absorptivity at 400 nm of 150 L/(mol·cm) or higher, and (C) photochromic compound.

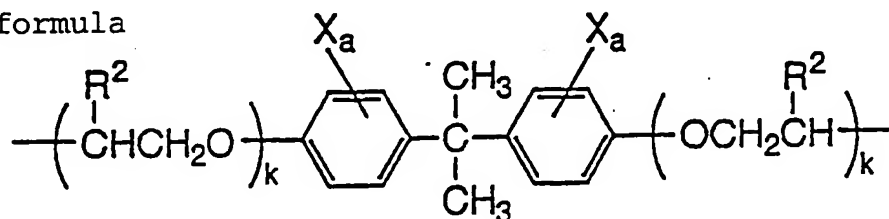
There is no special limitation on the type of radical-polymerizable monomer used in the manufacturing method of the photochromic product of curing of this invention, and any monomer having radical polymerizable groups may be used. Examples of the preferable types of radical polymerizable groups include acrylate groups, methacrylate groups and vinyl groups.

Examples of the radical polymerizable monomers that can be used preferably in this invention include the compounds represented by formulas (1), (2) and (3).

Diacrylate compounds and dimethacrylate compounds represented by the following formula (1)

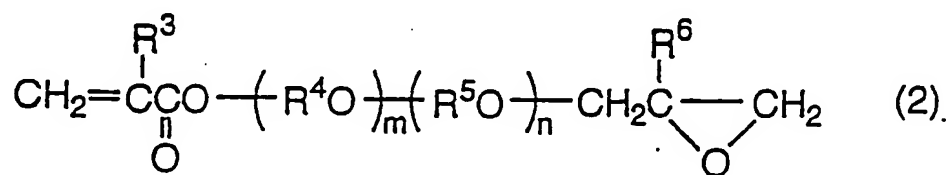


where each R^1 , which may be identical or equal to each other, represents a hydrogen atom or methyl group; A, which may be identical or different and may be substituted, represents an alkylene group, oxyalkylene group, or the group represented by the following formula

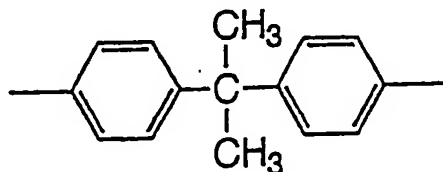


(where each R^2 represents a hydrogen atom or methyl group; X represents halogen atom; k is an integer in the range of 0-5; and a is an integer in the range of 0-4 representing the substitution number of the halogen atom) and n is an integer in the range of 1-20;

epoxy-group-containing acrylate compounds and methacrylate compounds represented by the following formula (2)

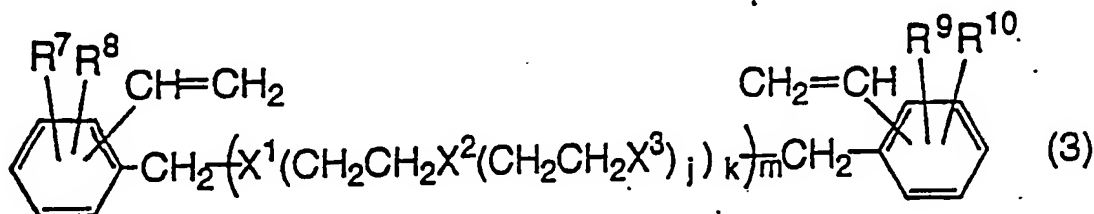


where, R^3 and R^6 , which may be identical or different from each other, represent a hydrogen atom or methyl group; R^4 and R^5 , which may be identical or different from each other and may be substituted, represent an alkylene group or a group represented by the following formula:



and m and n are 0 or 1.

Vinylbenzyl compounds represented by the following formula (3)



where, R^7 , R^8 , R^9 , and R^{10} , which may be identical or different from each other, represent halogen atoms; X^1 , X^2 , and X^3 represent oxygen atoms or sulfur atoms independently; j , k and m are 0 or 1; when $k = 0$, $j = 0$; when $m = 0$, $k = j = 0$; when $j = k = m = 1$, X^1 , X^2 , and X^3 cannot be sulfur atoms at the same time).

The following are specific examples of the radical polymerizable monomers that can be used preferably in this invention.

Examples of diacrylate compounds and dimethacrylate compounds include diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, butanediol dimethacrylate, hexamethylene dimethacrylate, bisphenol A

dimethacrylate,
 2,2-bis(4-methacryloyloxyethoxy-3,5-dibromophenyl)propane,
 2,2-bis(4-methacryloyloxyethoxyphenyl) propane,
 2,2-bis(4-methacryloyloxydiethoxyphenyl) propane,
 2,2,-bis(4-methacryloyloxytriethoxyphenyl) propane
 2,2-bis(4-methacryloyloxypentaethoxyphenyl) propane, etc.

Examples of the expoy-group-containing acrylate compounds and methacrylate compounds include glycidyl acrylate, glycidyl methacrylate, β -methylglycidyl acrylate, β -methylglycidyl methacrylate, bisphenol A monoglycidyl ether methacrylate, etc.

Examples of vinylbenzyl compounds include bis-4-vinylbenzyl ether, bis-4-vinylbenzylsulfide, 1,2-(p-vinylbenzyloxy)ethane, 1,2-(p-vinylbenzylthio)ethane, bis-(p-vinylbenzyloxyethyl)sulfide, etc.

In addition, as radical polymerizable monomers, it is possible to use unsaturated carboxylic acids, acrylic and methacrylic esters, fumaric ester, and aromatic vinyl compounds. Examples of the unsaturated carboxylic acid compounds include acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, and acrylic acid. Examples of methacrylic esters include methyl acrylate, methyl methacrylate, benzyl methacrylate, phenyl methacrylate, tribromophenyl methacrylate, 2-hydroxyethyl methacrylate, trifluoromethyl methacrylate, and urethane acrylate [sic; acrylate]. Examples of fumaric esters include monomethyl fumarate, diethyl fumarate, and diphenyl fumarate. Examples of the aromatic vinyl compounds include styrene, chlorostyrene, α -methylstyrene, vinyl naphthalene, isopropenyl naphthalene, bromostyrene, divinylbenzene, etc. These radical polymerizable monomers may be used either alone or as a mixture of several types.

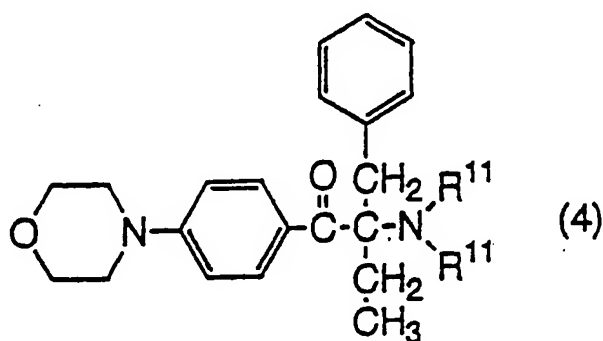
In consideration of the durability and coloration/discoloration and other properties of the photochromic product of curing formed in photopolymerization of the mixture of a photochromic compound and a radical polymerizable monomer to be explained later, among the aforementioned radical polymerizable monomers, the radical polymerizable monomer mixture prepared from the diacrylate compound or dimethacrylate compound represented by formula (1) and the epoxy-group-containing acrylate compound or methacrylate represented by formula (2) is preferred.

According to this invention, it is necessary to use a UV-polymerization initiator having a main absorption in the UV region and having a molar light absorptivity at 400 nm of 150 L/(mol·cm) or higher. It is undesirable to use a photopolymerization initiator having the main absorption in the visible region of 400 nm or longer, because it has color itself, i.e., there are colors in the stage before the photochromic property is displayed. Even when the main absorption is in the UV region, if the molar light absorptivity at 400 nm is less than 150 L/(mol·cm), in the irradiation by an active energy radiation having a main spectrum longer than 400 nm on the light-emission spectrum, it is difficult to carry out cleavage, and it is hard to obtain the product of curing in a short time. That is, as the photochromic compound usually absorbs the UV light in the range of 380-400 nm and turns color, it is hard to absorb the active energy radiation in the range of 380-400 nm to carry out cleavage, and it is impossible to complete the polymerization in a short time. In order to complete the polymerization, the active energy radiation should radiate for a long time, leading to deterioration of the photochromic compound.

The UV-polymerization initiators can be roughly divided into the self-cleavage UV-polymerization initiators and hydrogen-extracting type UV-polymerization initiators. The latter UV polymerization initiator is usually used together with a photosensitizer. Amine compounds are usually used as the photosensitizer. When these amine compounds are used, the initial coloration of the polymer is significant. Consequently, it is preferred that the self-cleavage UV-polymerization initiator be used. In order to obtain a colorless and transparent product of curing, among the self-cleavage UV-polymerization initiators, it is preferred to use α -aminoalkylphenone UV-polymerization initiators, acylphosphine oxide UV-polymerization initiator, and bisacylphosphine oxide type UV-polymerization initiators can be adopted preferably.

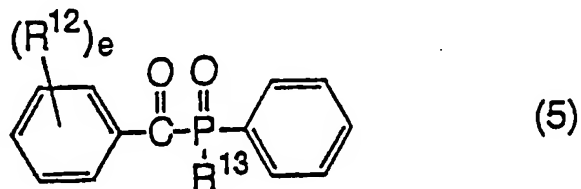
There is no special limitation on the type of the aforementioned preferable UV-polymerization initiators. Typical compounds are those represented by the following formulas (4), (5) and (6).

α -aminoalkylphenone compounds represented by the following formula (4):



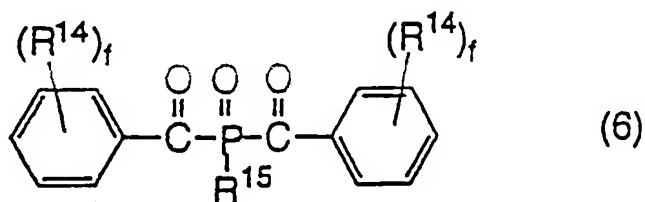
where, each R^{11} , which may be identical or different from each other, represents a methyl group or ethyl group.

Acylphosphine oxide compounds represented by following formula (5):



where, each R^{12} , which may be identical or different from each other, represents a methyl group, methoxy group, or chlorine atom; e represents 2 or 3; and R^{13} represents a phenyl group or methoxy group.

Bisacylphosphine oxide compounds represented by the following formula (6):



where, each R^{14} , which may be identical or different from each other, represents a methyl group, methoxy group, or chlorine atom; f is 2 or 3; and R^{15} represents a 2,4,4-trimethylpentyl group.

According to this invention, the following are specific examples of the UV-polymerization initiators that can be used preferably as the UV-polymerization initiator having the main absorption in the UV region and having molar light absorptivity at 400 nm of 150 L/(mol·cm) or higher.

α -aminoalkylphenone photopolymerization initiators:

- (1) 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone

Acylphosphine oxide photopolymerization initiators:

- (1) 2,6-dimethylbenzoyldiphenylphosphine oxide
- (2) 2,4,6-trimethylbenzoyldiphenylphosphine oxide
- (3) 2,6-dichlorobenzoyldiphenylphosphine oxide
- (4) 2,6-dimethoxybenzoyldiphenylphosphine oxide

Bisacylphosphine oxide photopolymerization initiators:

- (1) bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylepentylphosphine oxide
- (2) bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide
- (3) bis(2,4,6-trimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide
- (4) bis(2,6-dichlorobenzoyl)-2,4,4-trimethylpentylphosphine oxide

These UV-photopolymerization initiators may be used either alone or as a mixture of several types.

The added amount of the UV-polymerization initiator depends on the polymerization conditions and type of initiator, as well as the type and composition of the radical polymerizable monomer, and there is no way to define it generally. Usually, with respect to 100 parts by weight of the radical polymerizable monomer, the amount of UV-polymerization initiator added should be in the range of 0.01-1 part by weight, or preferably in the range of 0.05-1 part by weight. When the amount is over 1 part by weight, the internal uniformity of the obtained polymer is poor, and the tone also deteriorates. On the other hand, when the added amount is less than 0.01 part by weight, it is impossible to realize a sufficient curing degree.

In addition to these UV-polymerization initiators, it is also possible to add a thermal polymerization initiator. The conventional thermal polymerization initiator can be added without any restriction. Examples of the thermal polymerization initiators include benzoyl peroxide, lauroyl peroxide, and other diacyl peroxides; t-butyl peroxyneodecanate, and other peroxy esters; diisopropyl peroxydicarbonate, and other percarbonates; azobisisobutyronitrile, and other azo compounds; etc.

There is no special limitation on the type of the photochromic compound contained in the photopolymerization composition used in this invention. Any photochromic compound having absorption for coloration in the visible region can be used. Specific examples of the [photochromic compounds with] absorption in the visible region include the photochromic compounds having an absorption near 400-480 nm and displaying a color tone in the range from yellow to orange; the photochromic compounds having an absorption near 480-550 nm and displaying color tone in the range from red to violet; and the photochromic compounds having an absorption near 550-600 nm and displaying a color tone in the range from violet to blue. These photochromic compounds may be used either alone or as a mixture of several types to realize the so-called intermediate colors, such as gray, brown, amber, etc., as the color tone.

Examples of the photochromic compounds that can be used preferably in this invention include chromene compounds, fulgides or fulgimide compounds, and spirooxazine compounds.

There is no special limitation on the chromene compounds. Any conventional compound having a chromene skeleton and photochromic property can be used. The following are some examples of the chromene compounds:

- (1) 2,2-diphenyl-7-octoxy (2H) benzo (f) chromene
- (2) spiro(bicyclo(3,3,1)nonane-9,2'-(2H)benzo(h)chromene)
- (3) spiro(norbornane-2,2'-(2H)benzo(h)chromene)
- (4) 7'-methoxyspiro(bicyclo(3,3,1)nonane-9,2'-(2H)benzo(h)chromene)
- [5] 7'-methoxyspiro(norbornane-2,2'-(2H)benzo(h)chromene)
- [6] 2,2-dimethyl-7-octoxy(2H)benzo(f)chromene

There is no special limitation on the fulgide compounds. Any conventional compound having a fulgide skeleton and photochromic property can be used. The following are some examples of the fulgide compounds:

- (1) N-methyl-6,7-dihydro-4-methylspiro(5,6-benzo(b)thiophene dicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- (2) N-cyanomethyl-6,7-dihydro-4-methyl-2-phenylspiro(5,6-benzo(b)thiophenedicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- (3) N-cyanomethyl-6,7-dihydro-4-methyl-2-(p-methoxyphenyl)spiro(5,6-benzo(b)thiophenedicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- (4) N-cyanomethyl-6,7-dihydro-4-methylspiro(5,6-benzo(b)thiophene dicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- (5) N-cyanomethyl-6,7-dihydro-4-cyclopropylspiro(5,6-benzo(b)thiophenedicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- (6) 6,7-dihydro-N-methoxycarbonylmethyl-4-methyl-2-phenylspiro(5,6-benzo(b)thiophenedicarboxyimido-7,2-tricyclo(3,3,1,1)decane

There is no special limitation on the spirooxazine compounds. Any conventional compound having a spirooxazine skeleton and photochromic property can be used. The following are some examples of the spirooxazine compounds:

- (1) 1,3,3-trimethylspiro(indole-2,3-(3,2-a)(1,4)naphthooxazine)
- (2) 1,3,3-trimethyl-6'-piperidinospiro(indole-2,3-(3,2-a)(1,4)naphthooxazine)
- (3) 6-fluoro-1'-methyl-8"-methoxy-6"-morpholino dispiro(cyclohexane-1,3'-(3H)indole-2'-(2'H),3"-(3H)naphtho(3,2-a)(1,4)oxazine)
- (4) 1-methoxycarbonylmethyl-8"-methoxy-6"-(4-methylpiperazino) dispiro(cyclohexane-1,3'-(3H)indole-2'-(2'H),3"-(3H)naphtho(3,2-a)(1,4)oxazine)
- (5) 1'-(2-(dioxane-2-yl)ethyl)-6"-morpholinodispiro(cyclohexane-1,3'-(3H)indole-2'-(2'H),3"-(3H)naphtho(3,2-a)(1,4)oxazine)
- (6) 5-fluoro-1'-methyl-6"-piperadinodispiro(cyclohexane-1,3'-(3H)indole-2'-(2'H),3"-(3H)naphtho(3,2-a)(1,4)oxazine)
- (7) 8"-methoxydispiro(cyclohexane-1,3'-(3H)indole-2'-(2'H),3"-(3H)naphtho(2,3-a)(1,4)oxazine)

The added amount of the photochromic compound should be selected appropriately corresponding to the density of coloration. Usually, with respect to 100 parts by weight of the radical polymerizable monomer, the added amount of the photochromic compound should be in the range of 0.001-1.0 part by weight, or preferably in the range of 0.01-0.5 part by weight. If the added amount of the photochromic compound is less than 0.001 part by weight, it is impossible to realize a sufficient coloration density, and the durability of the photochromic characteristics deteriorate. When the amount is over 1.0 part by weight, it is hard to complete the polymerization in a short time. This is undesired.

As needed, it is possible to add various stabilizers and additives to the photopolymerizable composition of this invention, such as mold-release agents, UV absorbents, UV stabilizers, oxidation inhibitors, static inhibitors, fluorescent inhibitors, fluorescent dyes, dyes, pigments, perfumes, etc.

As the light source used for photopolymerization in this invention, any active energy radiation having a main light emission spectrum at 400 nm or longer, that is, in the visible spectral range, may be used. Examples of the light sources that can be used include metal halide lamps, medium-pressure mercury lamps, high-pressure mercury lamps, ultrahigh-pressure mercury lamps, sterilizing lamps, xenon lamps, tungsten lamps, etc. When a metal halide lamp, high-pressure mercury lamp, or other lamp that also emits UV light in addition to the visible light is used, it is necessary to use a UV-reduction filter, etc., to cut off or reduce the active energy radiation in the UV region.

Usually, as the photochromic compound absorbs UV light in the range of 380-400 nm and turns color, the colored photochromic compound absorbs the active energy radiation intended for cleavage of the photopolymerization initiator, so that cleavage is difficult to take place, and it is impossible to complete the polymerization in a short time. When the active energy radiation is irradiated for a longer time to complete the polymerization, deterioration in the photochromic compound occurs. Consequently, when the light source also emits UV light, a UV-reduction filter, etc., can be used to cut off or reduce the active energy radiation in the UV region so as to inhibit coloration of the photochromic compound. In this way, it is possible to use a light source with a spectrum containing UV light. However, in the practical curing operation, there is no need to completely cut off the spectral portion with wavelength shorter

than 400 nm from the light source. As long as the light-emission spectrum at 400 nm or longer is the main spectrum, the active energy radiation may also contain the UV active energy radiation at a wavelength shorter than 400 nm. In this case, although the photochromic compound is weakly colored by the UV active energy radiation and a portion of the active energy radiation is absorbed, the active energy radiation at 400 nm or longer can substantially transmit through it, so that the UV-polymerization initiator can be cleaved, and polymerization curing can be carried out well.

The irradiation time depends on the wavelength and intensity of the light source, and the shape and structural ingredients of the product of curing. Consequently, it is preferred that the irradiation time be determined by means of preliminary experiments, etc.

When the photopolymerization is carried out, at least the side of the mold under irradiation of light has to be transparent. Usually, this portion is made of glass, etc. In particular, it is preferred that fused silica glass or other material transparent to UV light be used. There is no special limitation on the type of the material, as long as it is transparent. Also, in the molding operation, it is possible to carry out polymerization while pressure is applied from the exterior.

For the manufacturing method of this invention, it is possible to adopt the conventional injection polymerization method. In a typical method, the photopolymerizable composition is injected into dies held together by an elastomer gasket or a spacer; then, the aforementioned active energy radiation is irradiated for curing. The molding is then taken out.

The photochromic product of curing formed using the method of this invention may be subject to the following processing or secondary treatment corresponding to the specific application. For example, it may be dyed using a disperse dye, etc., and it may be subject to antireflection processing, static-inhibiting processing, etc., by coating a hard coating agent mainly comprising a silane-coupling agent, as well as silicon, zirconium, antimony, aluminum, tin, tungsten, or another sol component, or by depositing a film of SiO_2 , TiO_2 , ZrO_2 , or another metal oxide, or by coating an organic polymer film.

By adopting the manufacturing method using the photopolymerization method of this invention, it is possible to obtain, in a short time, a photochromic product of curing free of deterioration of the photochromic compound, having high coloration density, and sufficient hardness. Under sunlight or light emitted from a mercury lamp, the obtained product of curing is transformed from a colorless state to a colored state, and the change is reversible, with an excellent light-modulating effect. Consequently, the obtained product of curing can be used as organic glass having photochromic property, in such applications as photochromic lenses, etc.

Application examples

In the following, this invention will be explained in more detail with reference to application examples. However, this invention is not limited to these application examples. In the application examples, "parts" refers to "parts by weight."

The radical polymerizable monomers used in the following application examples are listed below:

- M1: 2,2-bis(4-methacryloyloxyethoxyphenyl) propane
- M2: 2,2-bis(4-methacryloyloxydiethoxyphenyl) propane
- M3: 2,2-bis(4-methacryloyloxypentaethoxyphenyl) propane
- M4: bisphenol A-monoglycidyl ether methacrylate
- M5: triethylene glycol dimethacrylate
- M6: tetraethylene glycol dimethacrylate
- M7: hexamethylene dimethacrylate
- M8: glycidyl methacrylate
- M9: 2-hydroxyethyl methacrylate
- M10: methyl methacrylate
- M11: isobornyl acrylate
- M12: pentaerythritol triacrylate hexamethylene

diisodiisocyanate urethane prepolymer

The photochromic compounds in the application examples are listed below:

Chromene compounds:

- C1: 2,2-diphenyl-7-octoxy(2H)benzo(f)chromene
- C2: spiro(bicyclo(3,3,1)nonane-9,2'-(2H)benzo(h)chromene)

Fulgide compounds:

- F1: N-methyl-6,7-dihydro-4-methylspiro(5,6-benzo(b)thiophenedicarboxyimido-7,2-tricyclo(3,3,1,1)decane
- F2: N-cyanomethyl-6,7-dihydro-4-methyl-2-phenylspiro(5,6-benzo(b)thiophene dicarboxyimido-7,2-tricyclo(3,3,1,1)decane

Spirooxazine compounds:

S1:

1,3,3-trimethylspiro(indole-2,3-(3,2-a)(1,4)naphthooxazine)

S2: 1,3,3-trimethyl-6'-piperidinospiro(indole-2,3-(3,2-a)(1,4)naphthooxazine)

The photopolymerization initiators used in the application examples are listed below. The number in () refers to the molar light absorptivity (L/(mol·cm)) at 400 nm.

I1: CGI-1700 (commercial name: product of Ciba Geigy Japan Co., Ltd.)

A 1:3 mixture of
bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylbenzylphosphine oxide (550) and 2-hydroxy-2-methyl-1-phenylpropane-1-one (10 or lower)
I2: 2,4,6-trimethylbenzoyldiphenylphosphine oxide (250)
I3: 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone (200)

I4: methylbenzoylformate (10 or lower)

Application Example 1

90 parts 2,2-bis(4-methacryloyloxydiethoxyphenyl propane), 10 parts glycidyl methacrylate, as well as a photochromic compound and photopolymerization initiator with amounts listed in Table I were well blended. The blend liquid was injected into dies consisting of a glass panels and a gasket made of ethylene-vinyl acetate copolymer. A UV-reduction filter, which can cut off the following proportions of the active energy radiation:

380 nm : 99%、390 nm : 98%、4
00 nm : 50%、410 nm : 15%

is placed between a metal halide lamp and the dies to ensure that the active energy radiation for irradiation has a wavelength substantially longer than 400 nm. The metal halide lamp has an output power of 120 W/cm, and the irradiation time is 15 min. After completion of the polymerization, the product of polymerization was taken out from the glass dies.

Curability

For assessing the curability of the obtained product of curing (with thickness 2 mm), photopolymerization was carried out under the same conditions but without adding the photochromic compound. The hardness results were compared with each other to assess the curability. The grades are defined as follows.

(O) Curing is identical to that of the product of polymerization without adding the photochromic compound (100-90%)

(Δ) Hardness is in the range of 90-50% of that of the product of polymerization without adding the photochromic compound

(X) Hardness is 50% or lower than that of the product of polymerization without adding the photochromic compound

Coloring performance

In order to assess the coloring performance of the product of polymerization obtained, the following test was carried out: The product of polymerization was colored by irradiation for 30 sec by light emitted from a Hamamatsu Photonics Xenon Lamp L-2480 (300 W)

SHL-100 through an Aero Mass Filter (product of Corning Inc.) at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$, with radiation intensity on the surface of the product of polymerization of 2.4 mW/cm^2 at 365 nm and $24 \text{ }\mu\text{W/cm}^2$ at 245 nm. The light absorptivity at the maximum absorptive wavelength based on the coloration of the photochromic compound was assessed by a percentage (%) with respect to the light absorptivity of the product of polymerization prepared by injecting a mixture prepared by blending well 1.0 part of a thermal polymerization initiator (t-butyl peroxyneodecanate) in place of the photopolymerization initiator into the same dies, followed by slowly heating up from 30°C to 90°C in 18 h and then maintaining at 90°C for 2 h in an air oven. The grades are defined as follows.

(O) When the light absorptivity percentage is 80% or higher

(Δ) When the light absorptivity percentage is in the range of 80-50%

(X) When the light absorptivity percentage is 50% or lower

In addition, the tone after coloration of the product of polymerization by setting under sunlight for 10 min was assessed by visual observation. The results are listed in Table I.

Table I.

| | ① クロメン 化合物N.o. | ② フキト又はフキト 化合物N.o. | ③ スピロサジン 化合物N.o. | ④ 開始剤 | ⑤ フイター | ⑥ 硬化性 | ⑦ 発色性能 | ⑧ 発色色調 |
|-----------|----------------------|--------------------------|------------------------|-------------|-----------|----------|-----------|-----------|
| ⑨ 実施例1 | C1 (0.04) | — | — | I2 (0.1) | 有 | ○ | ○ | 黄 ⑬ |
| | — | F1 (0.04) | — | I1 (0.2) | 有 | ○ | ○ | 赤 ⑭ |
| | C1 (0.04) | — | S2 (0.02) | I3 (0.2) | 有 | ○ | ○ | グレー ⑮ |
| | C1 (0.10) | F2 (0.03) | — | I1 (0.2) | 有 | ○ | ○ | ブラウン |
| | C2 (0.15) | — | S1 (0.20) | I1 (0.4) | 有 | ○ | ○ | ブラウン ⑯ |
| | C2 (0.07) | F1 (0.07) | — | I2 (0.1) | 有 | ○ | ○ | ブラウン |
| 比較例1 | C1 (0.04) | — | — | I4 (0.1) | 有 | × | — | — |
| 比較例2 | C1 (0.04) | — | — | I4 (0.1) | 無 | × | — | — |
| 比較例3 | | F1 (0.01) | | I1 (0.2) | 無 | ○ | × | 赤 ⑭ |

⑩

| | | |
|------|----|-----------------------------------|
| Key: | 1 | Chromene compound No. |
| | 2 | Fulgide or fulgimide compound No. |
| | 3 | Spirooxazine compound No. |
| | 4 | Initiator |
| | 5 | Filter |
| | 6 | Curing property |
| | 7 | Coloring performance |
| | 8 | Tone of coloration |
| | 9 | Application Example |
| | 10 | Comparative Example |
| | 11 | Yes |
| | 12 | No |
| | 13 | Yellow |
| | 14 | Red |
| | 15 | Gray |
| | 16 | Brown |

Application Example 2

The operation was carried out in the same way as in Application Example 1, except that the types of the photochromic compound and the radical polymerizable monomer were changed from those used in Application Example 1. The results are listed in Table II.

Table II

| ラジ加単量体 No. | クロメン 化合物No. | フガド又はフガシド 化合物No. | スピオキサジン 化合物No. | 開始剤 | 硬化性 | 発色性能 | 発色色調 |
|---|----------------|---------------------|-------------------|-------------|-----|------|----------------------|
| M1:(50) M3:(40) M8:(10) | C1 (0.10) | F2 (0.05) | — | I1 (0.2) | ○ | ○ | グレー ⁽¹⁰⁾ |
| M5:(40) M6:(40) M12:(10) M8:(10) | C1 (0.20) | — | S2 (0.08) | I1 (0.2) | ○ | ○ | ブラウン ⁽¹¹⁾ |
| M1:(40) M6:(55) M9:(5) | C1 (0.15) | F2 (0.08) | — | I1 (0.2) | ○ | ○ | グレー ⁽¹⁰⁾ |
| M4:(20) M6:(50) M10:(20) M8:(10) | C2 (0.05) | — | S2 (0.05) | I1 (0.2) | ○ | ○ | グレー ⁽¹⁰⁾ |
| M1:(60) M11:(30) M8:(10) | C2 (0.10) | F2 (0.07) | — | I2 (0.1) | ○ | ○ | ブラウン ⁽¹¹⁾ |
| M5:(60) M7:(15) M2:(20) M8:(5) | C1 (0.15) | — | S2 (0.08) | I2 (0.1) | ○ | ○ | グレー ⁽¹⁰⁾ |

④
実施例2

| | |
|--------|-----------------------------------|
| Key: 1 | Radical polymerizable monomer No. |
| 2 | Chromene compound No. |
| 3 | Fulgide or fulgimide compound No. |
| 4 | Spirooxazine compound No. |
| 5 | Initiator |
| 6 | Curing property |
| 7 | Coloring performance |
| 8 | Tone of coloration |
| 9 | Application Example |
| 10 | Gray |
| 11 | Brown |
| 12 | Gray |

Comparative Example 1

The operation was carried out in the same way as in Application Example 1, except that methylbenzoylformate was used as the photopolymerization initiator. The results are listed in Table I.

Comparative Example 2

The operation was carried out in the same way as in Application Example 1, except that methylbenzoylformate was used as the photopolymerization initiator, and the UV-reduction filter was not used. The results are listed in Table I.

Comparative Example 3

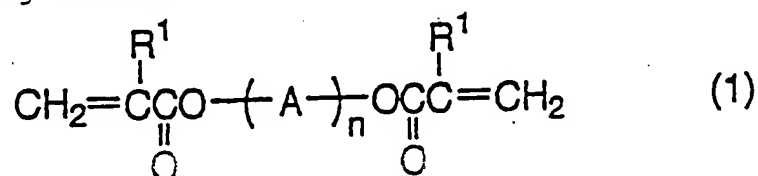
The operation was carried out in the same way as in Application Example 1, except that the UV-reduction filter was not used. The results are listed in Table I.

Claims

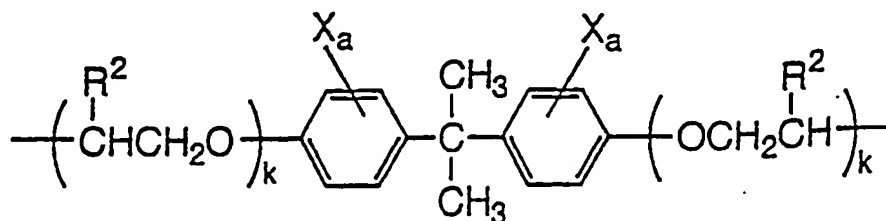
1. A process for the production of a photochromic product of curing, characterized by the fact that curing is realized by irradiating an active energy radiation having a light-emission spectrum on a photopolymerizable composition containing (A) radical polymerizable monomer, (B) UV-light polymerization initiator having the main absorption in the UV region and having a molar light absorptivity at 400 nm of 150 L/(mol·cm) or higher, and (C) photochromic compound.

2. The process described in Claim 1, characterized by the fact that radical polymerizable monomer (A) refers to at least one type of compound selected from the following compounds:

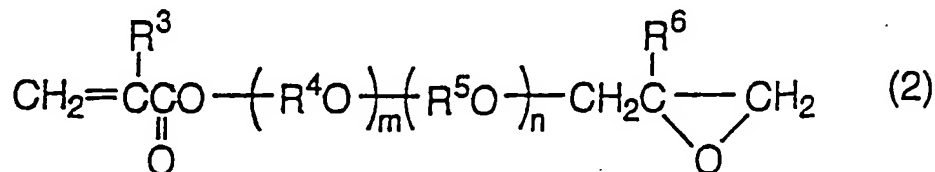
diacrylate compounds and dimethacrylate compounds represented by the following formula (1)



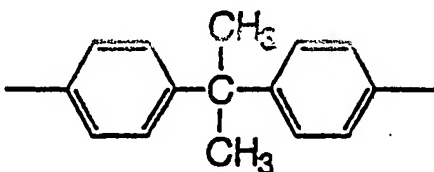
where, each R^1 , which may be identical or equal to each other, represents a hydrogen atom or methyl group; each A, which may be identical or different from each other and may be substituted, represents an alkylene group, oxyalkylene group, or the group represented by the following formula



(where, R^2 represents a hydrogen atom or methyl group; X represents a halogen atom; k is an integer in the range of 0-5; and a is an integer in the range of 0-4 representing the substitution number of the halogen atom) and n is an integer in the range of 1-20; epoxy-group-containing acrylate compounds and methacrylate compounds represented by the following formula (2)

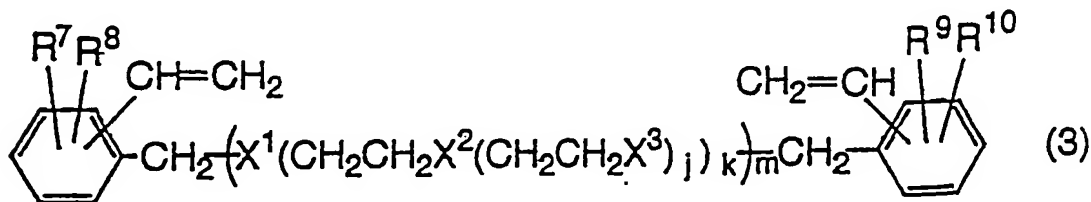


where, R^3 and R^6 , which may be identical or different from each other, represent a hydrogen atom or methyl group; R^4 and R^5 , which may be identical or different from each other and may be substituted, represent an alkylene group or group represented by the following formula:



and m and n are 0 or 1;

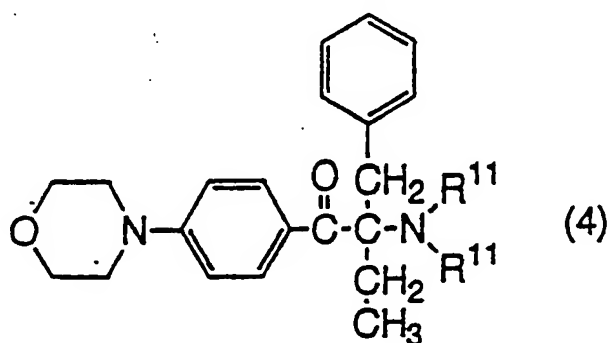
vinylbenzyl compounds represented by the following formula (3)



where, R^7 , R^8 , R^9 , and R^{10} , which may be identical or different from each other, represent halogen atoms; X^1 , X^2 , and X^3 represent oxygen atoms or sulfur atoms independently; j , k and m are 0 or 1; when $k = 0$, $j = 0$; when $m = 0$, $k = j = 0$; when $j = k = m = 1$, X^1 , X^2 , and X^3 cannot be sulfur atoms at the same time).

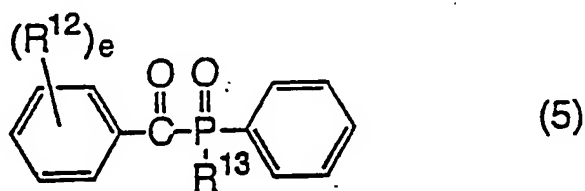
3. The process described in Claim 1, characterized by the fact that UV-polymerization initiator (B) refers to at least one type of compound selected from the following compounds:

compounds represented by the following formula (4):



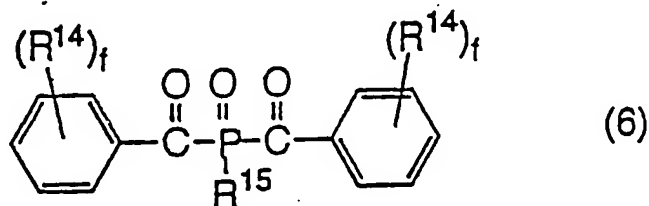
where, each R^{11} , which may be identical or different from each other, represents a methyl group or ethyl group;

compounds represented by the following formula (5):



where, each R^{12} , which may be identical or different from each other, represents a methyl group, methoxy group, or chlorine atom; e represents 2 or 3; and R^{13} represents a phenyl group or methoxy group;

and compounds represented by the following formula (6):



where, each R^{14} , which may be identical or different from each other, represents a methyl group, methoxy group, or chlorine atom; f is 2 or 3; and R^{15} represents a 2,4,4-trimethylpentyl group.

4. The process described in Claim 1, characterized by the fact that the amount of UV-polymerization initiator (B) used with respect to 100 parts by weight of radical polymerizable monomer (A) is in the range of 0.01-1 part by weight.

5. The process described in Claim 1, characterized by the fact that photochromic compound (C) is selected from the group of chromene compounds, fulgide compounds, fulgimide compounds, and spirooxazine compounds.

6. The process described in Claim 1, characterized by the fact that the amount of photochromic compound (C) used with respect to 100 parts by weight of radical polymerizable monomer (A) is in the range of 0.001-1.0 part by weight.

7. The process described in Claim 1, characterized by the fact that the active energy radiation is irradiated through a filter that cuts off the UV light with a wavelength shorter than 400 nm.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01384

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁶ C09K9/02, C08F2/46, C08K5/15, C08L33/14, G02C7/02,
G03C1/73

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl.⁶ C09K9/02, C08F2/46, C08K5/15, C08L33/14, G02C7/02,
G03C1/73

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| P, A | JP, 7-292011, A (Tokuyama Corp.), November 7, 1995 (07. 11. 95) & EP, 681018, A2 & AU, 9516590, A | 1 - 7 |
| A | JP, 7-134356, A (Sekisui Chemical Co., Ltd.), May 23, 1995 (23. 05. 95) (Family: none) | 1 - 7 |
| A | JP, 4-358117, A (Tokyo Keikaku K.K.), December 11, 1992 (11. 12. 92) (Family: none) | 1 - 7 |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

August 15, 1996 (15. 08. 96)

Date of mailing of the international search report

August 27, 1996 (27. 08. 96)

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